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Structural disorder and short-range order in full Heusler alloys Fe_2VAl and Co_2CrAl from first principles calculations

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HIGHLIGHTS

- The ordered Fe_2VAl is a non-magnetic narrow-gap semiconductor.
- The ordered Co_2CrAl is a ferromagnetic semimetal.
- Disordered Fe_2VAl is magnetic metal.
- Disordering of Co_2CrAl decreased its magnetization by 32%.
- Short range order raised magnetization in Fe_2VAl but not in Co_2CrAl.

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ABSTRACT

Heusler alloys are intensively studied and applied in various spintronic devices. First principles calculations of their electronic structure allow to predict promising compounds with high spin polarization. However the theoretical predictions usually substantially deviate from experimental data. One of the reason is incorrect structural models used in the calculations. Heusler alloys are apt to form various disordered modifications with high concentration of antisite defects. In this paper we considered the effects of structural order and disorder on the electronic structure, stability and magnetic properties of full Heusler alloys Fe_2VAl and Co_2CrAl. The ordered Fe_2VAl is non-magnetic narrow-gap semiconductor, the ordered Co_2CrAl is a ferromagnet with metal behavior for majority spin band and narrow-gap semiconductor for minority one. When disordering Fe_2VAl becomes a ferromagnetic metal. Co_2CrAl loses minority band gap and its spontaneous magnetization reduces by 32%. Introduction of short range order in the disordered structure by increasing the portion of clusters specific for bcc structure further raised the magnetization in Fe_2VAl and did not change it in Co_2CrAl.

1. Introduction

Heusler X_2YZ alloys (X, Y are transition metals, Z is a *p*-element) are considered as promising materials for spintronics due to their capability to produce spin-polarized currents [13]. They can demonstrate metallic behavior for one of the spin bands and the semiconducting behavior for another. First principal prediction of new composition of Heusler alloys with spin polarization is of great interest. The main challenges for these studies are the electronic correlations effects associated with transition metals [4,5] and the tendency of the materials to form disordered phases with various types of defective structures [6–9]. Both the aspects are of great importance. In this study we tried to focus on the structural factor and consider the influence of disordering on electronic and magnetic properties calculated from standard DFT framework. As a representative example we studied two compounds, namely Fe_2VAl and Co_2CrAl, with alternative behavior in their basic ordered structural state.

Fe_2VAl is a nonmagnetic semimetal [10] or narrow gap semiconductor [11]. The pseudogap at the Fermi level [12] is reproduced in calculations using various functionals, including hybrid [13] or the DFT + U method [14]. The ordered Co_2CrAl alloy is magnetic and has complete spin polarization near the Fermi level: the subband of electrons with spins directed along the magnetization vector ("spin up") is filled, and the subband with opposite spin direction ("spin down") is empty [15–17]. The experimentally determined value of the spontaneous

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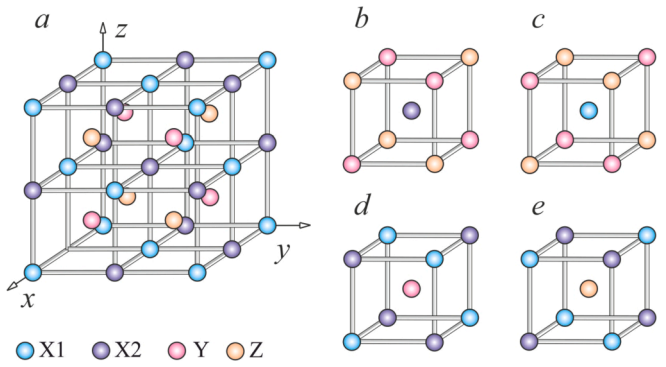

Fig. 1. The unit cell of ordered X_2YZ (*a*) and the types of the nearest environment of the lattice sites (*b-e*).

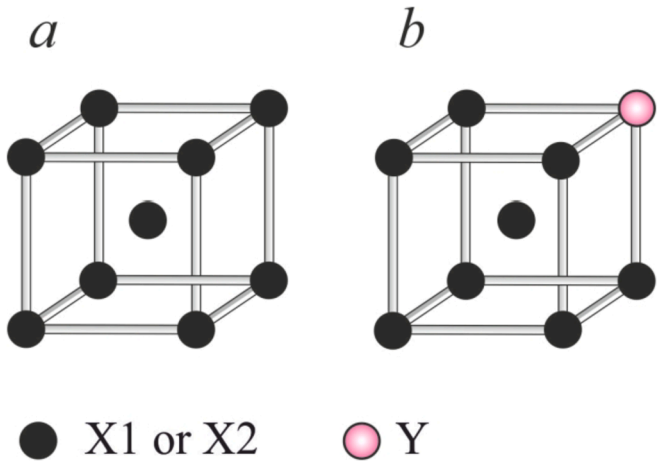

Fig. 2. Elementary clusters of atoms X used for simulation of the short-range order in the disordered alloy: (*a*) complete cluster and (*b*)c luster with the Y atom in one of the vertexes. The configuration data is obtained from the original cluster of structure $L2_1$ shown in Fig. 1*d*.

magnetization varies from 1.53 to 1.62 μ_B [17,18] while calculations for an ordered alloy give 3 μ_B [17,19,20]. A decrease in the magnetization for the disordered Co_2CrAl alloy was observed in the experiments [18, 19] but was not considered in the calculations for the corresponding disordered structural models.

The structure of the ordered alloys Fe_2VAl and Co_2CrAl is of $L2_1$ type (Fig. 1a). X atoms occupy the sites of two fcc sublattices displaced relative to each other by a half-period along one of the coordinate axes. Y and Z atoms occupy the interstices of the X sublattices. The first coordination sphere of the X sites contains four Y and four Z sites (Fig. 1*b*, 1*c*). Disordering is achieved by the introduction of antisite defects, when atoms of one of the sublattices are replaced by atoms of the other sublattice and vice versa. The disorder changes the initial types of the nearest environment of atoms (Fig. 1*b-d*), which should affect the features of the electronic structure and properties of the alloys. Formally, antisite defects can be arranged between all three pairs of sublattices of the original ordered alloy, and substitutions of atoms in one, two, or three pairs of sublattices can be present in the structure.

The interchangeable atoms can be located in the sublattices stochastically or form the short range order distribution. In the first case, the probability to find a replaced atom in any site of the sublattice does not depend on its local environment and is equal for all the sites. The short range order is generated by the restriction of the possible local configurations in the disordered structures. Some of them can be energetically preferable and stabilizes the defect structure of disordered state. Another types on the contrary increase the total energy of the

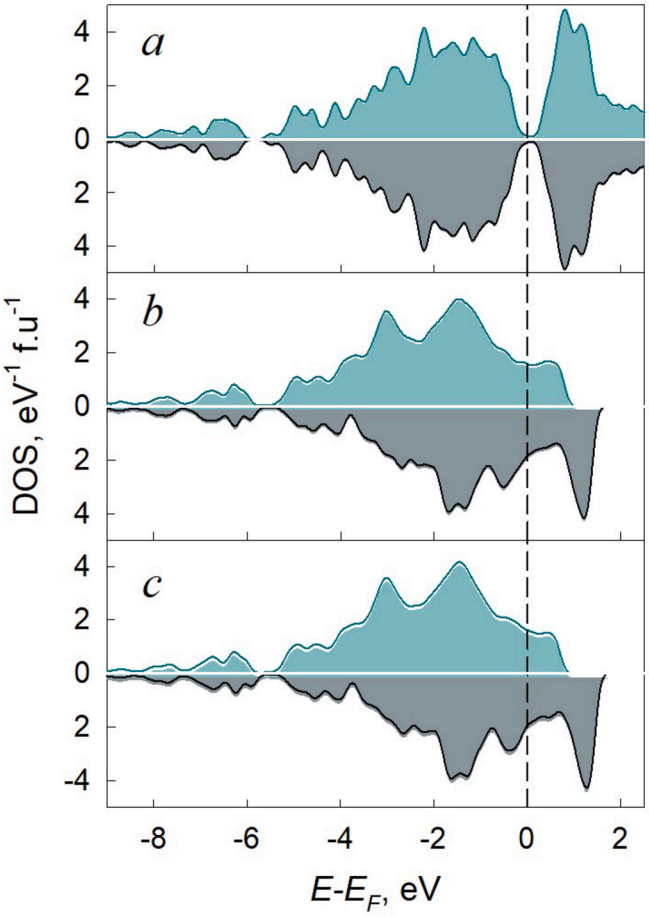

Fig. 3. Density of states for Fe_2VAl alloy calculated for (*a*) the ordered structure, (*b*) the disordered structure with stochastically distributed antisite defects on Y and X sublattices, and (*c*) the disordered structure with short-range order.

compound and should be minimized in the structure model used in the calculation. In the case of magnetic materials special attention should be paid to the specific cluster configuration that can induce FM or AFM ordering.

We considered three structural models of the X_2YZ alloy: (*a*) the case of an ideal ordered structure (all the atoms are in their native sublattices), (*b*) partially disordered structure with stochastically distributed antisite defects, and (*c*) partially disordered model with a specific type of the short range order. Disordering was generated by antisite defects between the sublattices of *d*-elements X and Y so that the resulting structure was close to $D0_3$ structure typical for ferromagnetic Fe_3Si and Fe_3Al. Our short range order model is aimed at maximization the number of $D0_3$-based local configuration as compared with the model of stochastic distribution.

2. Calculation details

The calculations of the total energy, electronic structure, and magnetic moments were carried out in the framework of the density functional theory [20] using the basis of plane waves and pseudopotentials. Exchange-correlation effects were taken into account by PBE version [21] of the generalized gradient approximation (GGA) for the pseudopotentials. Quantum ESPRESSO package [22] was used for high performance calculations. Structural optimization was performed within BFGS quasi-newton algorithm. Both unit cell volume and atomic positions in the cells were relaxed.

To generate disorder and short range order in the standard *ab initio* technique we used supercell method [23]. The unit cell of the ordered

Table 1
Calculation data for Fe_2VAl. Values for different structures are given per Fe_2VAl formula unit.

Structure	Relaxed cell parameter, Å	Majority density of states at the Fermi level	Minority density of states at the Fermi level	Total density of states at the Fermi level	Total magnetization, μ_B	Spin polarization at the Fermi level	Cohesive energy, eV
Perfectly ordered	5.69	0	0	0	0	0	−20.05
Disordered with stochastical distribution of defects	5.71	1.59	1.85	3.44	2.1 ± 0.1	−0.08	−19.30 ±0.02
Disordered with short range order	5.71	1.62	1.96	3.58	2.5 ± 0.1	−0.10	−19.32 ±0.02

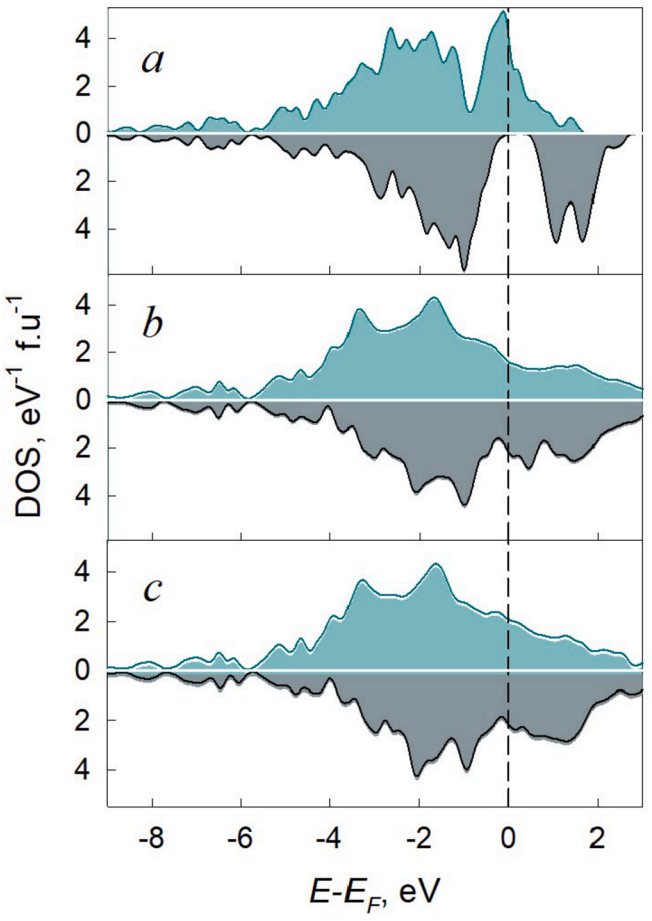

Fig. 4. Density of states for Co_2CrAl alloy calculated for (*a*) the ordered structure, (*b*) the disordered structure with stochastically distributed antisite defects on Y and X sublattices, and (*c*) the disordered structure with short-range order.

X_2YZ alloy with the $L2_1$ structure was expanded by a factor of 8 and contained 128 lattice sites, i. e. 32 nodes for X1, X2, Y, and Z sublattices. For the supercells we used $2 \times 2 \times 2$ *k*-point mesh and 50 Ry energy cuttoff.

In our structural models for the disordered X_2YZ alloys 50% of Y atoms took part in the formation of antisite defects with both X1 and X2 sublattices. When the defects are introduced into the X and Y sublattices, clusters of elements X appear in the structure, which are characteristic of the bcc and $D0_3$ structures and initially absent in the $L2_1$ type (Fig. 2*a*). The short-range order is taken into account by increasing the share of such clusters in the disordered structure compared to the model of stochastic distribution. After the maximum possible number of complete clusters in the supercell was reached the remaining number of defects was distributed in the manner that only one vertex of the X cluster was replaced with element Y (Fig. 2*b*).

From the *ab initio* electronic structure calculations we derived and consider the following parameters to characterize the structures: density of states at the Fermi level, spin polarization at the Fermi level, the total magnetization, and the cohesive energy. Spin polarization *P* was estimated by the formula:

$$P = \frac{N_\uparrow(E_F) - N_\downarrow(E_F)}{N_\uparrow(E_F) + N_\downarrow(E_F)},$$

where $N_\uparrow(E_F)$ and $N_\downarrow(E_F)$ are the densities of states of electron at the Fermi level for majority and minority gap, respectively. The formula for calculation of cohesive energy E_{coh} was

$$E_{coh} = (E_{X2YZ} - N_X E_X - N_Y E_Y - N_Z E_Z)/N_{f.u.},$$

where E_{X2YZ} is the total energy of the X_2YZ alloy per unit cell or supercell, E_X, E_Y, and E_Z are the total energies of the individual atoms X, Y, and Z, respectively, N_X, N_Y, and N_Z are the numbers of these atoms in the cell or supercell, $N_{f.u.}$ – the number of X_2YZ formula units in the unit cell ($N_{f.u.} = 4$) or supercell ($N_{f.u.} = 32$). The energies of individual atoms were found as the energies of simple cubic structures whose sites were distant enough from each other in order to eliminate the interaction between them. All the values E_{X2YZ}, E_X, E_Y and E_Z were calculated taking into account the effect of spin polarization.

3. Results and discussion

Fig. 3 shows the distribution of density of states calculated for Fe_2VAl with ordered structure (*a*), disordered alloy with a stochastic distribution of defects (*b*), and with short-range order (*c*). In Table 1 the corresponding values of the spin polarization at the Fermi level, the

Table 2
Calculation data for Co_2CrAl. Values for different structures are given per Co_2CrAl formula unit.

Structure	Relaxed cell parameter, Å	Majority density of states at the Fermi level	Minority density of states at the Fermi level	Total density of states at the Fermi level	Total magnetization, μ_B	Spin polarization at the Fermi level	Cohesive energy, eV
Perfectly ordered	5.70	5.62	0	5.62	3.0	1	−18.44
Disordered with statistical distribution of defects	5.77	1.60	2.17	3.77	2.1 ± 0.1	−0.15	−18.09 ±0.02
Disordered with short range order	5.77	2.07	2.18	4.25	2.1 ± 0.1	−0.03	−18.05 ±0.02

magnetization, and the cohesive energy are presented. The ordered phase is semiconductor with a narrow band gap of 0.13 eV, which explains the relatively low conductivity value [11]. The effects of spin polarization do not appear, and the compound is nonmagnetic. Magnetic moments of all the atoms in the structure are zero and no AFM ordering was detected.

Under disordering the alloy becomes metal with high density of states at the Fermi level for both « spin-up» and «spin-down » electrons which makes it possible to expect a significant increase in conductivity. The disordered state is spin-polarized with magnetization 2.1 ± 0.1 μ_B/f.u, which is connected with the formation of magnetic clusters (Fig. 2*a*) that can be found also in the structures of ferromagnetic α-Fe (bcc structure), Fe_3Si and Fe_3Al ($D0_3$ type). An increase in the portion of these clusters in the modification with the short-range order led to a further advance in the magnetization up to 2.5 ± 0.1 μ_B/f.u.

At the same time, the proposed type of short-range order is close in energy to the model of the stochastic distribution of defects in a disordered alloy and does not provide significant energy gain. The distribution of the density of states was almost unchanged (Fig. 3*b* and *c*). A slight change in the density of states (from 3.44 to 3.58) and spin polarization (from −0.08 to −0.10) at the Fermi level was observed.

The densities of states calculated for three structural models of Co_2CrAl similar to Fe_2VAl, are shown in Fig. 4. In Table 2 the values of spin polarization at the Fermi level, magnetization, and cohesive energy are presented. The ordered structure has a half-metal behavior [24] in agreement with previous studies [19] with an integer magnetization of 3.0 μ_B/f.u. and minority band gap of 0.66 eV. Under disordering the alloy lost the minority band gap. However the total density of states at the Fermi level dropped by 33% because of descent in density for majority band. The magnetization decreased by 32% as compared with the ordered state. The short range order did not influenced on magnetization but changed the polarization at the Fermi level due to increase of density for majority band.

As in the case of Fe_2VAl, the disordered state is energetically unfavorable. The change in energy owing to the introduction of short-range order is insignificant and comparable to the error of the supercell method. Note that in both cases the ordered phases have lower cohesive energies than the disordered ones which corresponds to the general consideration that the ordered phases are low temperature ones. The disordered state can be thermodynamically at equilibrium at higher temperatures when the entropy contribution to the free energy becomes larger.

In the ordered structure of Fe_2VAl, none of the atoms has a magnetic moment. In the ordered Co_2CrAl all the elements contribute to the magnetization (the magnetic moments of Co, Cr, and Al are 0.73, 1.75, and −0.17 μ_B/f.u, respectively). When Fe_2VAl is disordered, the appearance of spontaneous magnetization is caused by clusters of iron atoms. In the disordered Co_2CrAl the decrease in magnetization is probably due to a violation of symmetry in the local environment of the lattice cites. Our calculations qualitatively confirmed the trend of diminution of the magnetic moment in Co_2CrAl during disordering. Nevertheless the 50% replacement of chromium by cobalt is not enough to achieve the exact experimental values. Real samples of the disordered phases apparently have a more complex structure compared to the model we used. For instance, the presence of vacancies may also have an effect on the magnetization and electronic structure [25]. In addition to the antisite defects between X and Y sublattices, X and Z, as well as Y and Z sublattices can also exchange with atoms to form B_2 and bcc (A_2) types of structure [20].

4. Conclusion

In this paper we studied the effect of structural disorder and short-range order on the electronic structure and magnetic properties of full Heusler alloys Fe_2VAl and Co_2CrAl with initial $L2_1$ type of ordered structure. According to the standard DFT calculations the ordered Fe_2VAl is non-magnetic semiconductor with narrow band gap of 0.13 eV. In the case of Co_2CrAl a significant spin polarization was found. The compound is metal for majority band and semiconductor with gap of 0.66 eV for minority band.

To understand the influence of structural disorder we generated supercells and simulated antisite defects between the sublattices Fe and V in Fe_2VAl, and Co and Cr in Co_2CrAl. In both cases the disordered structures have higher cohesive energies and can be equilibrium phases at the temperatures lower than that for the ordered ones. Antisite defects in initially nonmagnetic Fe_2VAl caused spin polarization and appearance of a magnetization equal to 2.1 ± 0.1 μ_B/f.u. Introduction of the short range order in the disordered Fe_2VAl alloy by increasing of the fraction of the clusters specific for bcc structure enhanced spontaneous magnetization up to 2.5 ± 0.1 μ_B/f.u. In the magnetic Co_2CrAl alloy antisite defects decreased magnetization from 3.0 to 2.1 ± 0.1 μ_B/f.u. Short range order did not changed its value. In both alloys the proposed structural model of short range order almost did not affect the cohesive energy and DOS curves.

Generally our calculations demonstrated the significant impact of antisite defects on the properties of Heusler alloys. First principals calculation must be based on the correct structural models to carefully predict the parameteres important for the practical use. Disorder in the Fe and V sublattices in Fe_2VAl turned the material from non-magnetic semiconductor into ferromagnetic metal. Accounting for the antisite defects in Co and Cr sublattices in Co_2CrAl partially compensated the discrepancy between the theoretical value of spontaneous magnetization calculated for the ordered structure and the experimental value measured for the actually disordered samples.

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References

[1] Heusler alloys, in: C. Felser, A. Hirohata (Eds.), Springer Series in Materials Science, vol. 222, Springer International Publishing Switzerland, 2016, 486 pp.
[2] A. Hirohata, K. Takanashi, J. Phys. D Appl. Phys. 47 (2014) 193001.
[3] C. Felser, B. Hillebrands, J. Phys. D Appl. Phys. 40 (2007) 1507.
[4] O. Kristanovski, et al., Phys. Rev. B. 95 (2017), 045114.
[5] S. Chadov, et al., J. Phys. D Appl. Phys. 42 (2009), 084002.
[6] J.C.G. Tedesco, et al., J. Phys. Condens. Matter 28 (2016) 476002.
[7] J. Minár, J. Braun1, S. Bornemann, H. Ebert, M. Donath, J. Phys. D Appl. Phys. 42 (2009), 084009.
[8] B. Pradines, et al., Phys. Rev. B 95 (2017), 094425.
[9] V. Jung, et al., J. Phys. D Appl. Phys. 42 (2009), 084007.
[10] C.-S. Lue, J.H. Ross Jr., Phys. Rev. B 58 (1998) 9763.
[11] S. Nishino, et al., Phys. Rev. Lett. 79 (1997) 1909.
[12] H. Okamura, et al., Phys. Rev. Lett. 84 (2000) 3674.
[13] D.I. Bilc, P. Ghoswz, Phys. Rev. B. 83 (2011) 205204.
[14] D. Do, M.-S. Lee, S.D. Mahanti, Phys. Rev. B 84 (2011) 125104.
[15] T. Block, M.J. Garey, B.A. Gurney, O. Jepsen, Phys. Rev. B 70 (2004), 205 114.
[16] M. Zhang, et al., J. Magn. Magn. Mater. 277 (2004) 130.
[17] N.I. Kourov, et al., Phys. Solid State 55 (2013) 977.
[18] A.D. Svyazhin, et al., J. Exp. Theor. Phys. 116 (2013) 452.
[19] Y.V. Kudryavtsev, et al., Phys. Rev. B 77 (2008) 195104.
[20] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) A1133.
[21] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[22] P. Giannozzi, et al., J. Phys. Condens. Matter 29 (2017) 465901.
[23] M.C. Payne, et al., Rev. Mod. Phys. 64 (1992) 1045.
[24] M. Rostami, Surf. Sci. 674 (2018) 103.
[25] Enamullah, D.D. Johnson, K.G. Suresh, A. Alam, Phys. Rev. B 94 (2016) 184102.